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ARTICLE

Enhanced Lead and Zinc Removal via Prosopis Cineraria Leaves Powder: A Study on Isotherms and RSM Optimization

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ABSTRACT

This study investigates the potential of Prosopis cineraria Leaves Powder (PCLP) as a biosorbent for removing lead (Pb) and zinc (Zn) from aqueous solutions, optimizing the process using Response Surface Methodology (RSM). Prosopis cineraria, commonly known as Khejri, is a drought-resistant tree with significant promise in environmental applications. The research employed a Central Composite Design (CCD) to examine the independent and combined effects of key process variables, including initial metal ion concentration, contact time, pH, and PCLP dosage. RSM was used to develop mathematical models that explain the relationship between these factors and the efficiency of metal removal, allowing the determination of optimal operating conditions. The experimental results indicated that the Langmuir isotherm model was the most appropriate for describing the biosorption of both metals, suggesting favorable adsorption characteristics.

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Additionally, the D-R isotherm confirmed that chemisorption was the primary mechanism involved in the biosorption process. For lead removal, the optimal conditions were found to be 312.23 K temperature, pH 4.72, 58.5 mg L⁻¹ initial concentration, and 0.27 g biosorbent dosage, achieving an 83.77% removal efficiency. For zinc, the optimal conditions were 312.4 K, pH 5.86, 53.07 mg L⁻¹ initial concentration, and the same biosorbent dosage, resulting in a 75.86% removal efficiency. These findings highlight PCLP's potential as an effective, eco-friendly biosorbent for sustainable heavy metal removal in water treatment.

Keywords: Prosopis Cineraria; Lead; Zinc; Isotherms; Optimization

1. Introduction

Research has demonstrated that hazardous material releases and their environmental spread can have catastrophic consequences for people who are exposed^[1]. The enormous rise in the use of heavy metals over the last few decades has led to an increase in the flow of metallic materials into the aquatic environment^[2]. These metals' primary attribute is their persistence due to their non-degradable nature. Moreover, the majority of metal ions are harmful to living organisms^[3]. Therefore, before wastewater is disposed of, harmful elements should be eliminated in order to provide a pollution-free environment.

Toxic metal ions can be extracted from aqueous solutions using a variety of techniques, such as chemical precipitation, ion exchange, membrane processes, reverse osmosis, solvent extraction, evaporation, and adsorption^[4, 5]. However, using the majority of these techniques has several drawbacks, such as the need for expensive machinery and space, the creation of sludge and other hazardous pollutants, and the need for electricity. These conventional methods could potentially have a number of drawbacks. For example, preparatory treatment may be necessary to eliminate complex compounds that could hinder precipitation. The minimal solubility of different metals in a mixed waste stream typically occurs at different pH values during precipitation. Therefore, the pH value at which the solubility of one element is too high may be the site of greatest removal of that metal. Furthermore, a successful precipitation process might not be the best way to address wastewater treatment issues given the increasingly strict treatment and disposal laws^[6].

Many investigations have been conducted recently on the adsorption of heavy metals by various compounds. The development of non-traditional, low-cost adsorbents for the removal of metals from aqueous solutions, such as industrial and natural wastewater has been extensively documented.

Numerous studies have thoroughly examined the ability of different leaf materials. In the present study, the Leaves Powder of Prosopis cineraria were used to study the chemical form of the metal, solution pH, duration of contact, metal concentration, presence of competing adsorbates, amount of sorbent, organic matter, temperature, particle size, optimization methods, and other factors that influence the adsorbability of dissolved elements^[7–9].

2. Methodology

2.1. Sorbent

The Prosopis cineraria leaves as showed in Figure 1 from Oman's Dhofar Region, which were gathered from the Salalah region, were carefully processed. They were first thoroughly cleaned with distilled water to get rid of any impurities or debris. After being cleaned, the leaves were dried and ground into a fine powder using a home grinder. To guarantee complete moisture removal, the leaves were dried at 60 °C for 24 hours. Prior to usage, the dried leaves were sieved through a standard screen to produce a homogeneous particle size. The particle diameters varied between 75 and 212 μ m.



Figure 1. Prosopis cineraria Leaves before and after drying.

2.2. Chemicals

Lead and zinc concentrations were generated by melting the relevant salts in distilled water and adjusting the pH with less hydrochloric acid and base.

2.3. Experimentation

To prepare the lead, and zinc solution, the pH value was reduced to 5.1 with HCl and NaOH, which were obtained by diluting the stock solution. To test the effect of agitation time on early lead and zinc levels, a mixture of 30 mL of metal solution and 0.1 g of 75 μ m biosorbent was stirred at 180 rpm for a period of one hour. Centrifugation was performed at predetermined intervals, and the balance of lead and zinc in the solution was measured using AAS fitted with a hollow cathode and acetylene flame. Subsequent experiments used the same spectrophotometric approach. The amount of metal absorbed by Prosopis cineraria leaves was calculated using the following equation (Equation (1)): the difference between the initial metal amount given to the powder material and the ion concentration for the supernatant.

$$q = (C_0 - C_f) * (V/M)$$
 (1)

In the framework of metal adsorption, the parameter q (mg g⁻¹) represents the weight of metal consumed per unit mass of adsorbent. The parameters C_0 and C_f denote the metal's starting and ultimate concentrations, calculated in parts per million (ppm). V is the quantity of the solution in milliliters (mL), and M is the mass of the material that absorbs it in grams (g).

2.4. Isotherms of Biosorption

Biosorption isotherms explain how the absorbed metal ions and adsorbent material achieve equilibrium. Equilibrium isotherms are used to analyze the ability of Prosopis cineraria leaves to absorb lead and zinc metal ions. The Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich models are some of the most commonly employed to characterize such systems. These models are useful tools for analysing the kinetics of metal ion adsorption on biosorbents such as Prosopis cineraria leaves.

2.5. CCD

Using full factorial rotatable central composite design (CCD), the impact of several process factors, including temperature (X1), solution pH (X2), biosorbent dosage (X3), and initial metal concentration (X4), on the removal of lead and zinc metal from aqueous solutions was investigated^[10]. Thirty experiments were needed in total: sixteen cube point runs, eight axial point runs, and two center point runs. Each experiment had to be completed in duplicate. Every experiment was run with a constant agitation speed of 180 rpm and a contact time (t).

Using Equation (2)^[11], all independent variables were coded to five levels as Xi.

$$\mathbf{x}_{i} = \frac{X_{i} - X_{oi}}{\Delta X_{i}}, \ i = 0, 1, 2, 3, \dots k$$
 (2)

Where x_i is the real value of an independent variable, x0i is the real value of the independent variable at the center point, Δx_i is the step change, and X_i is the dimensionless value of an independent variable. Using STATISTICA 6.0 (Stat Soft Inc.), a second-degree polynomial equation (Equation (3)) was created to calculate the percentage of metal biosorption at various biosorption process operating conditions.

$$\begin{split} Y &= b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 \\ &+ b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 \\ &+ b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 \\ &+ b_{23} X2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4 \end{split} \tag{3}$$

Where, Y is the predicted response, X_1 , X_2 , X_3 and X_4 are independent variables: b_0 is an offset term; b_1 , b_2 , b_3 and b_4 are linear effects; b_{11} , b_{22} , b_{33} and b_{44} are squared effects; and b_{12} , b_{13} , b_{14} , b_{23} , b_{24} and b_{34} are interaction terms.

3. Results

3.1. Isotherms for Biosorption

3.1.1. Isotherm of Langmuir

This sorption model, given by him in reference^[12], served to estimate the biosorbent's maximal ion sorption capacity. This isotherm may be stated as follows in Equation (4):

$$q_{eq} = \frac{q_{\max}K_a C_{eq}}{1 + K_a C_{eq}} \tag{4}$$

To fit the experimental results, the Langmuir model was linearized, with " q_{max} " representing the biosorbent's monolayer biosorption capacity measured in mg g⁻¹ and the Langmuir constant " K_a " (L mg⁻¹) corresponding to the energy of biosorption as given in the Equation (5).

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_{\max}} + \frac{1}{K_a q_{\max}} \tag{5}$$

The relationship of sorption (C_{eq}/q_e) versus concentration (C_{eq}) show this removal follows Langmuir, as shown in **Figures 2** and **3** (Equation (5)). Experimental data for lead, zinc ion sorption on PCLP at various temperatures confirm this conclusion. **Tables 1** and **2** shows the Langmuir constants: saturated monolayer sorption capacity (q_{max}) and sorption stability constant (K_a) for lead and zinc ion sorption onto PCLP at 303, 308, 313, and 318 K. The (R^2) values clearly imply the lead, zinc ion sorption on PCLP follows isotherm. Notably, the maximal ion removal (q_{max}) was found to be 31.98 mg g⁻¹ and 27.66 mg g⁻¹ respectively, which gradually decreased as the temperature increased.



Figure 2. The Langmuir isotherm of lead adsorption by the PCLP biosorbent at different temperatures.



Figure 3. Langmuir isotherm for zinc by PCLP biosorbent at different temperatures.

3.1.2. Freundlich

The isotherm of Freundlich^[13] as given in Equation (6):

$$q_e = K_F C_{eq}^{\frac{1}{n}} \tag{6}$$

The formula can be transformed by using logarithmic values to determine the variables K_F and n as shown in Equation (7):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_{eq} \tag{7}$$

The constants were shown in **Tables 1** and **2**. **Figures 4** and **5** presents an exponential equation (Equation (7)).



Figure 4. The Freundlich isotherm of lead adsorption by the PCLP biosorbent at different temperatures.



Figure 5. Freundlich isotherm for zinc by PCLP biosorbent at different temperatures.

3.1.3. Temkin

Tempkin^[14] examined thermal properties for biosorption and the effect of adsorbate on biosorption isotherms. They argued that due to those interactions, the biosorption energy for all compounds falls linearly with coverage (**Figures 6** and **7**). The Tempkin isotherm has been applied in the form below as given in Equation (8).

$$q_{eq} = \frac{RT}{b} \ln(A_T C_{eq}) \tag{8}$$

And linearized as shown in Equation (9):

$$q_{eq} = B \ln A_T + B \ln C_{eq} \tag{9}$$



Figure 6. The Tempkin isotherm of lead adsorption by the PCLP biosorbent at different temperatures.



Figure 7. Tempkin isotherm for zinc by PCLP biosorbent at different temperatures.

3.1.4. Dubinin-Radushkevich

The equilibrium interaction between biosorption and adsorbate with a specific metal-powder partnership could be stated irrespective of temperature by using the removal ability (ϵ), as defined in Equation (10).

$$\varepsilon = \mathrm{RT}(1 + 1/\mathrm{C}_{\mathrm{eq}}) \tag{10}$$

The isotherm adopts a distinctive curve, and it is represented using Equation (11).

$$\ln q_e = \ln Q_{\rm D} - K \varepsilon^2 \tag{11}$$

This may be derived using (**Figures 8** and **9**) Equation (12):

$$\mathbf{E} = 1/\sqrt{2\mathbf{K}} \tag{12}$$

Drawing ln qe vs ε^2 , the Q_D & K are determined.



Figure 8. The Dubinin-Radushkevich isotherm of lead adsorption by the PCLP biosorbent at different temperatures.



Figure 9. Dubinin-Radushkevich isotherm for zinc by PCLP biosorbent at different temperatures.

Analysis of **Tables 1** and **2** reveals that the adsorption of lead, zinc on the PCLP exhibited strong correlations with different isotherms.

The equilibrium data were tested by all the four isotherm models. Based on the high correlation coefficient (R^2) values presented in **Tables 1** and **2** the best isotherm was determined. From these values, it was observed that Langmuir Isotherm with correlation coefficient of 0.998 fitted well followed by Freundlich, Tempkin and D-R isotherms with a correlation coefficient of 0.988, 0.969 and 0.843, respectively at a solution temperature of 303 K. For Zinc removal, the biosorption data was well represented by Langmuir model with correlation coefficient of 0.9943 followed by Freundlich, Tempkin and D-R isotherms with the correlation coefficient solution temperature of 0.9943 followed by Freundlich, Tempkin and D-R isotherms with the correlation coefficients

Tomporaturo		Langmuir			Freundlich			Tempkin			Dubinin Radushkevich			
T(K)	Ka, (L mg ⁻¹)	qmax (mg g ⁻¹)	\mathbb{R}^2	Kf, (mg g ⁻¹)	n	R ²	AT (L mg ⁻¹)	b	\mathbb{R}^2	QD (mg g ⁻¹)	K mol ² KJ ⁻²	E (KJ mol ⁻¹)	R ²	
304 308 313 318	0.06 0.18 0.33 0.65	31.9 26.93 25.90 25.57	0.99 0.996 0.990 0.991	2.86 5.67 7.38 9.72	1.62 2.28 2.56 2.94	0.988 0.992 0.962 0.988	0.667 2.344 4.392 10.382	354.3 485.9 524.4 575.6	0.969 0.965 0.992 0.969	17.881 18.037 19.735 20.731	0.0048 0.0091 0.0060 0.0034	10.1488 7.3779 9.0825 12.0554	0.843 0.802 0.896 0.959	

Table 1. Bisorption isotherm constants for lead removal with PCLP biosorbent.

Table 2. Bisorption isotherm constants for zinc removal using PCLP biosorbent.

T (Langmuir Isotherm			Freundlich Isotherm			Tempkin Isotherm			Dubinin Radushkevich Isotherm			
Temperature T(K)	qmax (mg g ⁻¹)	Ka, (L mg ⁻¹)	R ²	n	Kf, (mg g ⁻¹)	R ²	b	AT (L mg ⁻¹)	R ²	K mol ² KJ ⁻²	qmax (mg g ⁻¹)	R ²	E (KJ mol ⁻¹)
303	27.66	0.060	0.9943	1.721	2.535	0.978	412.18	0.59370	0.99456	0.00802624	15.82393	0.90332	8.89276
308	22.41297	0.133376	0.99808610	2.2679	4.14251	0.9740223	536.73	1.39623	0.99970	0.00289489	15.5751	0.88372	13.1422
313	21.12995	0.266304	0.99554364	2.882413	6.084599	0.9331284	658.78	3.94492	0.98770	0.01150483	16.51124	0.92702	6.59242
318	21.38628	0.573465	0.99831975	3.500519	8.424316	0.8678837	758.81	13.1665	0.95686	0.00459704	18.44433	0.9728	10.4291

of 0.9785, 0.99 and 0.903 respectively at a solution temperature of 303 K. At remaining temperatures also, the same type of trends was observed for both the metals.

4. Optimization of the Selected Biosorption Process Parameters Using RSM

It is extremely challenging to describe and simulate the biosorption process due to its high level of complexity and the interplay of numerous process factors. Although the one factor at a time approach is straightforward, it is unable to capture the interplay between all the variables that contribute to the biosorption process. It also necessitates a lengthy process and numerous experimental runs. Consequently, several processes were developed, enhanced, and optimized using the Response Surface Methodology (RSM). It provides details on the full interactions between all process parameters that have an impact on the process [15-18]. The percentage of metal biosorption and the metal absorption capacity of PCLP leaves biosorbent were found to be highly influenced by solution temperature, solution pH, initial concentration of metal, and biosorbent dosage, according to an analysis of preliminary experimental results. Thus, using full factorial rotatable central composite design (CCD), these four process variables were chosen to ascertain the ideal process parameters for the greatest removal of Lead and Zinc onto PCLP leaves biosorbent. Table 3 lists the levels and ranges of the selected independent factors that were employed in the metal removal studies.

To optimize the parameters, a 24-factorial CCD design

was utilized, consisting of eight axial points ($\alpha = -4$) and six replications at the center points (no = 6). This resulted in a total of thirty experiments (**Table 4** for lead and **Table 5** for zinc). The % elimination of lead and zinc (Y) was found to be a function of temperature (X1), pH (X2), biosorbent dosage (X3), and initial concentration (X4), according to the computed regression Equations (13) and (14) for the optimization of medium ingredients. Multiple regression analysis was performed on the experimental data, resulting in the following equations for lead (Y1) and zinc (Y2) biosorption:

$$\begin{split} &Y_1(\% \text{ Biosorption of Lead}) = -333.349 + \\ &21.237X_1 - 7.397X_2 + 17.138X_3 + 0.535X_4 \\ &-0.299X_1^2 - 2.209X_2^2 - 145.938X_3^2 - 0.007X_4^2 \\ &+0.516X_1X_2 - 0.035X_1X_3 - 0.003X_1X_4 \\ &+12.8X_2X_3 + 0.078X_2X_4 - 0.051X_3X_4 \end{split}$$

$$Y_{2}(\% Biosorption of Zinc) = -212.740$$

+12.065X₁ + 1.747X₂ + 67.310X₃ + 0.481X₄
-0.171X₁²-1.954X₂² + 34.332X₃²-0.003X₄² (14)
+0.574X₁X₂-2.085X₁X₃-0.005X₁X₄
+0.949X₂X₃ + 0.007X₂X₄-0.118X₃X₄

For lead and zinc, the regression model's coefficients were determined and are shown in **Tables 6** and **7**. They contain one block term, four linear, four quadratic and six interaction terms. The significance of each coefficient was determined by student's *t*-test and *p*-values and listed in **Table 6** for lead and **Table 7** for zinc. The relevant coefficient was more significant the bigger the t-value's magnitude and the smaller the p-value. As can be seen from their individual p-values (**Table 6** for lead and **Table 7** for zinc), this suggests that the linear, quadratic, and interaction effects of temperature, pH, biosorbent dosage, and initial concentration of lead are very significant. The parity plot (**Figure 10** for lead and **Figure 11** for zinc) showed a satisfactory correlation between the experimental and predicted values of percentage removal of lead indicating good agreement of model data with the experimental data.



Figure 10. A parity plot that displays the distribution of the actual versus projected lead biosorption % using PCLP.



Figure 11. A parity plot that displays the distribution of the actual against anticipated values for the zinc biosorption percentage using PCLP.

Table 8 displays the findings of the ANOVA-fitting second-order response surface model for lead and zinc. An accurate statistical tool for evaluating the model's significance and suitability is the Fisher variance ratio, or F-value (=SR²/Se²). The likelihood that the factors can sufficiently explain the variance in the data about its mean and that the estimated factor effects are real increases with the F-value above unity. Regression model ANOVA revealed an extremely low probability value (Pmodel > F = 0.000000) and a very significant model, as evidenced by the Fisher's F-test (Fmodel = 374.11 for Lead 718.5 for Zinc).

Furthermore, the F-value (F0.05(14.15) = SR^2/Se^2 = 374.11 for Lead and 718.5 for Zinc) computed at the 1% level was greater than the F-value (F0.05 (14.15) tabulars = 2.46 for both metals, demonstrating the significance of the treatment differences. An indicator of the model's variability in the observed response values is the correlation coefficient (R²). The stronger and more accurate the model's response prediction, the closer the R² value is to 1. The correlation coefficient values in this investigation (R² = 0.9979 for lead and 0.9985 for zinc) showed that the model could account for 99.79 percent (for lead) and 99.85% (for zinc) of the variability in the response. To further support the model's high significance, the adjusted correlation coefficient values (Adj R² = 0.9952 for lead and 0.9971 for zinc) were also extremely high^[19-23].

Figures 12-17 for lead and Figures 18-23 for zinc display the response surface plots of the percentage of lead biosorption vs the interactive effect of pH, beginning lead concentration, biosorbent dosage, and temperature. The 3D response surface graphs in Figures 12-17 for Lead and Figures 18-23 for Zinc visually represented regression Equations (13) and (14). By holding the values of the other variables constant, the response surface graphs display the relative effects of any two variables. Figure 12's response surface plot illustrates how temperature and solution pH interact when starting metal concentration and biosorbent dosage are maintained at midpoints.In a similar vein, the subsequent figures describe how various parameters interact to affect the proportion of metal biosorption^[24-26]. With one test parameter kept at zero, each response plot shows various combinations of the other two test parameters. The surface confined in the smallest curve (elliptical or circular) of the response plot represents the maximum percentage of biosorption of the level. Aqueous solution initial metal concentrations of 58.523 mg L^{-1} for lead and 53.07 mg L^{-1} for zinc, biosorbent dosages of 0.271 g L^{-1} for both lead and zinc, pH values of 4.72 for lead and 5.86 for zinc, and temperatures of 39.230C for lead and 39.420C for zinc are the ideal set of parameters for maximizing the percentage of biosorption of lead and zinc. Under these ideal circumstances, the percentage of lead and zinc that underwent biosorption was 83.77 and 75.66%, respectively. Table 8^[27-29] displays the ideal variable values for lead and zinc biosorption derived from the regression equation.

Independent Parameters	Range and Level						
	-2	-1	0	+1	+2		
(X_1) Temperature, °C	30.0	35.0	40.0	45.0	50.0		
(X ₂) Solution pH	3.0	4.0	5.0	6.0	7.0		
(X_3) Biosorbent Dosage, g L ⁻¹	0.10	0.20	0.30	0.40	0.50		
(X ₄) Initial metal concentration, mg L^{-1}	20.0	40.0	60.0	80.0	100.0		

Table 3. Range and concentrations of the independent parameters under experimentation for the biosorption of lead and zinc onto PCLP.

Experiments carried out under these ideal circumstances validated these conditions. The greatest percentage of biosorption for lead and zinc at these ideal conditions was found to be 80.23% and 72.31%, respectively. These experimental data clearly show that the experimental results correlate well with the outcomes predicted by the RSM. These findings also shown the effectiveness of applying statistical experimental designs utilizing RSM to optimize different parameters in order to enhance lead and zinc biosorption onto PCLP leaves biosorbent. These findings showed that a particular combination of temperature, solution pH, biosorbent dosage, and starting metal concentration led to the greatest percentage of metal biosorption.

Although this study shows that Prosopis cineraria Leaves Powder (PCLP) is a good biosorbent for removing zinc and lead, it should be noted that it has some limits. First off, the intricacies of continuous-flow systems, which are more prevalent in real-world applications, are not adequately captured by the batch trials carried out here. The scalability of PCLP biosorption in dynamic systems may be examined in future research. Additionally, real-world wastewater may contain a variety of pollutants that could impact biosorption effectiveness, even if the response surface methodology (RSM) made it possible to optimize process parameters.A more thorough grasp of PCLP's uses might be possible by investigating how well it performs in situations with several metals and organic contaminants. Lastly, even though the D-R isotherm indicated chemisorption as the main mechanism, additional molecular research might validate these interactions and investigate changes to improve the capacity and reusability of PCLP. According to the study's findings, PCLP has potential as an affordable, environmentally responsible method of treating water sustainably and supporting international initiatives to lessen heavy metal contamination. Pilot-scale testing and industry partnerships will be the next stages in incorporating this biosorbent into workable wastewater treatment systems.



Figure 12. Response surface plot showing how temperature and pH affect the amount of lead that PCLP is able to biosorb.



Figure 13. RSM plot showing how temperature and biosorbent dosage affect the proportion of lead that PCLP biosorbs.



Figure 14. RSM plot showing how temperature and starting metal concentration affect the percentage of lead that PCLP biosorbs.

	Values with Codes				Actual Numbers				% Sorption of Lead	
Kun No.	x1	x2	x3	x4	X1	X2	X3	X4	Noted	Expected
1	-1	-1	-1	-1	35	4	0.2	40	77.13	77.26292
2	-1	-1	-1	1	35	4	0.2	80	74.85	74.53125
3	-1	-1	1	-1	35	4	0.4	40	73.06	73.58292
4	-1	-1	1	1	35	4	0.4	80	71.13	71.26125
5	-1	1	-1	-1	35	6	0.2	40	65.67	65.75125
6	-1	1	-1	1	35	6	0.2	80	68.99	69.24958
7	-1	1	1	-1	35	6	0.4	40	67.59	67.19125
8	-1	1	1	1	35	6	0.4	80	71.19	71.09959
9	1	-1	-1	-1	45	4	0.2	40	69.15	69.50792
10	1	-1	-1	1	45	4	0.2	80	64.97	65.62625
11	1	-1	1	-1	45	4	0.4	40	65.76	65.75792
12	1	-1	1	1	45	4	0.4	80	62.1	62.28625
13	1	1	-1	-1	45	6	0.2	40	68.19	68.31625
14	1	1	-1	1	45	6	0.2	80	70.92	70.66458
15	1	1	1	-1	45	6	0.4	40	69.1	69.68625
16	1	1	1	1	45	6	0.4	80	72.32	72.44458
17	-2	0	0	0	30	5	0.3	60	56.7	56.8025
18	2	0	0	0	50	5	0.3	60	51.02	50.3925
19	0	-2	0	0	40	3	0.3	60	75.95	75.37917
20	0	2	0	0	40	7	0.3	60	73.98	74.02583
21	0	0	-2	0	40	5	0.1	60	78.91	78.6525
22	0	0	2	0	40	5	0.5	60	77.02	76.7525
23	0	0	0	-2	40	5	0.3	20	72.98	72.53917
24	0	0	0	2	40	5	0.3	100	72.65	72.56583
25	0	0	0	0	40	5	0.3	60	83.54	83.54
26	0	0	0	0	40	5	0.3	60	83.54	83.54
27	0	0	0	0	40	5	0.3	60	83.54	83.54
28	0	0	0	0	40	5	0.3	60	83.54	83.54
29	0	0	0	0	40	5	0.3	60	83.54	83.54
30	0	0	0	0	40	5	0.3	60	83.54	83.54

Table 4. The central composite design matrix displays both real and coded values for the proportion of lead biosorption with PCLP, in addition to the observed and anticipated values.

 $\overline{Note: X_1 = Temperature, X_2 = pH, X_3 = Biosorbent dosage, X_4 = Initial metal concentration.}$



Figure 15. RSM graphic showing how pH and biosorbent dosage affect the percentage of lead that PCLP is able to biosorb.



Figure 16. RSM plot showing how pH and starting metal concentration affect the percentage of lead that PCLP is able to biosorb.

D N	Values with Codes				Actual Numbers				% Sorption of Zinc	
Kun No.	x1	x2	x3	x4	X1	X2	X3	X4	Noted	Expected
1	-1	-1	-1	-1	35	5	0.2	40	69.2	69.50166
2	-1	-1	-1	1	35	5	0.2	80	58.38	58.39208
3	-1	-1	1	-1	35	5	0.4	40	66.13	66.44041
4	-1	-1	1	1	35	5	0.4	80	59.66	59.52833
5	-1	1	-1	-1	35	7	0.2	40	62.22	62.48542
6	-1	1	-1	1	35	7	0.2	80	60.12	60.19333
7	-1	1	1	-1	35	7	0.4	40	59.01	59.06167
8	-1	1	1	1	35	7	0.4	80	60.23	60.96708
9	1	-1	-1	-1	45	5	0.2	40	65.92	65.58542
10	1	-1	-1	1	45	5	0.2	80	60.21	60.40833
11	1	-1	1	-1	45	5	0.4	40	63.2	63.37667
12	1	-1	1	1	45	5	0.4	80	62.26	62.39708
13	1	1	-1	-1	45	7	0.2	40	59.29	59.67167
14	1	1	-1	1	45	7	0.2	80	63.22	63.31208
15	1	1	1	-1	45	7	0.4	40	56.71	57.10042
16	1	1	1	1	45	7	0.4	80	64.99	64.93833
17	-2	0	0	0	30	6	0.3	60	65.98	65.49625
18	2	0	0	0	50	6	0.3	60	65.72	65.55125
19	0	-2	0	0	40	4	0.3	60	49.12	49.11125
20	0	2	0	0	40	8	0.3	60	45.28	44.63625
21	0	0	-2	0	40	6	0.1	60	69.98	69.81125
22	0	0	2	0	40	6	0.5	60	68.86	68.37625
23	0	0	0	-2	40	6	0.3	20	68.93	68.48458
24	0	0	0	2	40	6	0.3	100	65.42	65.21291
25	0	0	0	0	40	6	0.3	60	75.82	75.82
26	0	0	0	0	40	6	0.3	60	75.82	75.82
27	0	0	0	0	40	6	0.3	60	75.82	75.82
28	0	0	0	0	40	6	0.3	60	75.82	75.82
29	0	0	0	0	40	6	0.3	60	75.82	75.82
30	0	0	0	0	40	6	0.3	60	75.82	75.82

Table 5. The central composite design matrix displays both real and coded values for the proportion of zinc biosorption with PCLP, in addition to the observed and anticipated values.

 $\overline{Note: X_1} = Temperature, X_2 = pH, X_3 = Biosorbent dosage, X_4 = Initial metal concentration.$



Figure 17. RSM map showing how the dosage of the biosorbent and the starting metal concentration affect the percentage of lead that is biosolated by PCLP.



Figure 18. Response surface map showing how temperature and starting metal concentration affect PCLP's zinc biosorption %.

Table 6. Quantum, t-worth and p-worth of lead onto PCLP.								
Parameter	Quantum	Worth	Error	t-Worth	p-Worth			
Constant	b_0	-333.349	11.90581	-26.4441	0.000000^{a}			
X_1	b_1	21.237	0.51757	50.8572	0.000000^{a}			
X_1^2	b ₁₁	-0.399	0.00479	-62.4747	0.000000^{a}			
X_2	b_2	-7.397	1.65237	-4.4766	0.000937^{a}			
${\rm X_2}^2$	b_{22}	-3.209	0.11982	-18.4394	0.000000^{a}			
X_3	b_3	17.138	14.36005	1.1934	00.357811			
X_{3}^{2}	b ₃₃	-145.938	11.98185	-12.1799	00.000000^{a}			
X_4	b_4	00.535	00.07180	7.4463	00.000013 ^a			
${\rm X_4}^2$	b 44	-00.007	00.00030	-22.9253	00.000000^{a}			
$X_1 * X_2$	b_{12}	00.516	00.02503	20.6159	00.000000^{a}			
$X_1 * X_3$	b_{13}	-00.035	00.25029	-0.1398	00.891317			
$X_1 * X_4$	b ₁₄	-00.003	00.00125	-2.2973	00.042231ª			
$X_2 * X_3$	b_{23}	12.800	01.25146	10.2280	00.000001 ^a			
$X_2 * X_4$	b_{24}	00.078	00.00626	12.4454	00.000000^{a}			
$X_3 * X_4$	b_{34}	00.051	00.06257	0.8190	00.430151			

Note: X_1 = Temperature, X_2 = pH, X_3 = Biosorbent dosage, X_4 = Initial metal concentration. ^a Significant (p ≤ 0.05), R² = 0.9979; Adj R² = 0.9952.

Table 7. Quantum, t-worth and p-worth of zinc onto PCLP.

Parameter	Quantum	Worth	Error	t-Worth	p-Worth
Constant	b_0	-267.206	13.30745	-20.0795	0.000000^{a}
X_1	b_1	6.723	0.40690	16.5229	0.000000^{a}
X_1^2	b_{12}	-0.101	0.00458	-22.0191	0.000000^{a}
X_2	b_2	76.544	1.75245	43.6781	0.000000a
${\rm X_2}^2$	b_{22}	-7.184	0.11452	-62.7337	0.000000^{a}
X_3	b_3	51.063	14.28647	3.5742	0.004363 ^a
X_{3}^{2}	b_{33}	-162.906	11.45168	-14.2255	0.000000^{a}
X_4	b_4	-0.796	0.07143	-11.1402	0.000000^{a}
${ m X_4}^2$	b_{44}	-0.005	0.00029	-19.1266	0.000000^{a}
$X_1 \ge X_2$	b_{12}	0.055	0.02392	2.3044	0.041709^{a}
$X_1 \ge X_3$	b_{13}	0.426	0.23922	1.7818	0.102366
$X_1 \ge X_4$	b_{14}	0.015	0.00120	12.3998	0.000000^{a}
$X_2 \ge X_3$	b_{23}	-0.906	1.19609	-0.7577	0.464566
$X_2 \ge X_4$	b_{24}	0.110	0.00598	18.4299	0.000000^{a}
$X_3 \ge X_4$	b_{34}	0.525	0.05980	8.7734	0.000003 ^a

 $\label{eq:Note: X1 = Temperature, X2 = pH, X3 = Biosorbent dosage, X4 = Initial metal concentration. a Significant (p \le 0.05), R^2 = 0.9985; Adj R^2 = 0.9971.$





Figure 19. RSM plot showing how the pH and starting metal concentration affect the proportion of zinc that PCLP is able to biosorb.

Figure 20. Response surface plot of the effects of initial metal concentration and biosorbent dosage on percentage of biosorption of zinc by PCLP.

Factor	Optimum of Lead	Optimum of Zinc
Temperature, °C	39.23	39.42
Solution pH	4.72	5.86
Biosorbent dosage, g	0.27	0.27
Initial metal concentration, mg L^{-1}	58.52	53.07
% Biosorption	83.77	75.86

Table 8. The variables with the best values were derived from regression models for PCLP's removal of lead and zinc.



Figure 21. Response surface plot of the effects of pH and temperature on percentage of biosorption of zinc by *Grewia Orbiculata* L.



Figure 22. Response surface plot of the effects of biosorbent dosage and temperature on percentage of biosorption of zinc by PCLP.



Figure 23. RSM graphic showing how pH and biosorbent dosage affect PCLP's zinc biosorption %.

5. Conclusions

The results of the experiment showed that the Langmuir isotherm model accurately characterized the biosorption of lead and zinc onto Prosopis cineraria Leaves Powder (PCLP), suggesting advantageous adsorption properties. The Dubinin-Radushkevich (D-R) isotherm's E values further revealed that the biosorption process primarily took place in the chemisorption region, just over the physisorption threshold. Response Surface Methodology (RSM) with a central composite design (CCD) was applied to optimize temperature, solution pH, biosorbent dosage, and initial metal ion concentration, among other important experimental parameters. The model's dependability was validated by the near alignment of the optimal conditions predicted by the RSM with the experimental data. At a temperature of 312.23 K, pH of 4.72, initial metal concentration of 58.5 mg L^{-1} , and biosorbent dosage of 0.27 g, the best removal efficiency of 83.77% was obtained for lead. Similar predictions were made for zinc, indicating a maximum removal efficiency of 75.86% at 312.4 K, pH 5.86, 53.07 mg L⁻¹ beginning metal concentration, and the same biosorbent dosage. These findings highlight PCLP's potential as an efficient biosorbent for heavy metal removal, offering a viable, long-term option for water treatment and environmental remediation.

Author Contributions

The authors of this study made the following contributions: R.N. conceptualized the research, designed the study, supervised the process, and contributed to data analysis and manuscript writing. G.B.R. conducted the experimental work; including the preparation of Prosopis cineraria Leaves Powder (PCLP) and performing biosorption experiments for lead and zinc removal. N.R.L. assisted in experimental design, data collection, analysis, and statistical modeling. N.M.S.Q. provided support in data analysis, result interpretation, and manuscript editing. N.P.B.S. performed statistical analysis using Response Surface Methodology (RSM) and contributed to mathematical model development. U.R.M. supported the experimental work, characterization of biosorbents, and manuscript writing. P.P.M. assisted with laboratory work, data collection, and interpretation of results. D.S.M.S.A.-K. contributed to the manuscript writing, especially discussing the ecological implications of using PCLP as a biosorbent. M.A.A.Q. provided insights into adsorption mechanisms and supported the manuscript's discussion. H.A.S.B.A. coordinated the study, reviewed results, and contributed to drafting and finalizing the manuscript.

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The data that support the findings of this study are available from the corresponding author upon reasonable request. All relevant data are included in the manuscript and its supplementary materials.

Conflicts of Interest

The authors declare no conflict of interest.

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